Synthetic Organic Chemicals

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The Preparation of Aldehydes

THE advent of synthetic resins and plastics has increased tremendously the interest in aldehydes. And since very few of the aldehydes are found in large quantities in nature, their preparation covers a wide field in synthetic organic chemistry.

The most general method of production is through oxidation of the corresponding primary alcohol. Chromic acid is used as the oxidizing agent, and the aldehyde is removed from the reaction mixture as soon as it is formed. The commercial practice is to pass a mixture of air and the alcohol over heated catalysts, such as copper, platinum, iron, etc. An analogous reaction, more appropriately termed dehydrogenation, in which the alcohol vapors are passed over copper, zinc, or brass, with the elimination of hydrogen, is very useful for the preparation of higher aliphatic aldehydes, such as isobutyraldehyde and normal or isovaleraldehyde, etc.

Oxidation of Hydrocarbons

Because of the large supply of aliphatic hydrocarbons available, direct partial oxidation would be a desirable commercial development but as yet such procedures are still in the experimental stage. However, benzaldehyde is produced in quantities, especially abroad, by oxidation of the aromatic hydrocarbon, toluene, using manganese and sulfuric acid as the reagents.

Olefines are reactive particularly at the double bond and will add ozone readily to form ozonides which are easily hydrolyzed to give aldehydes. In addition to its wide use in molecular structure determinations, this reaction has a commercial value in the preparation of certain compounds, such as vanillin from isoeugenol. Another application is the formation of picolinaldehyde by the ozonization and subsequent hydrolysis of the condensation product of alpha-picoline and benzaldehyde.

Reduction of Acids

Acids may be reduced indirectly by several methods to give the corresponding aldehyde or, in some cases, aldehyde containing one less carbon atom. Perhaps the oldest method is the dry distillation of the calcium or barium salts of aliphatic acids with those of formic acid. Like most dry distillations, however, the yields are poor; consequently the method is not used extensively. A more practical modification consists of passing the mixed acid vapors over zinc or manganese.

Sodium hypochlorite converts alpha-amino acids to N-chloroamino acids. The latter compounds lose hydrogen chloride to form the imino acids which hydrolyze readily to aldehydes. Similarly, when an alpha-hydroxy acid is oxidized with lead peroxide and sulfuric acid, the aldehyde is formed, with simul-

taneous elimination of a carbon atom. This decomposition of alpha-keto acids into the aldehydes is characteristic and is limited only by the availability of the keto acid or derivatives. Many of these keto acids may be obtained by condensation reactions such as Claisen's, in which ketones and ethyl chloroacetate form β-disubstituted glycidic acid esters which can be saponified and distilled. A simpler condensation of a ketone containing an active methylene group is that with ethyl formate in the presence of sodium ethoxide to give directly the sodium salt of the enol form of the aldehyde.

Reduction of Acid Chlorides

The conversion of the acid into the aldehyde without the loss of a carbon atom is accomplished by the reduction of the acid chloride by means of gaseous hydrogen, using palladium on barium sulfate as a catalyst, as developed by Rosenmund. The cost of the catalyst, however, practically restricts this method to laboratory preparations, such as 3-furaldehyde, gallaldehyde, etc. Stevens' method of converting the acid chloride to a substituted amide, then to the imido chloride by using phosphorous pentachloride, and finally reducing with stannous chloride, is a general procedure for making aldehydes.

Compounds containing two halogen atoms on the same carbon atom are readily hydrolyzed to the corresponding aldehyde. This reaction is the basis for the commercial preparation of benzaldehyde and p-chlorobenzaldehyde. Although it is not restricted to the aromatic series, the difficulty in procuring the proper aliphatic dihalogen compounds diminishes its usefulness.

Another form of hydrolysis, the simple addition of water to acetylene in the presence of mercury and sulfuric acid, is used in the technical production of acetaldehyde. This reaction is also general so far as the acetylenic derivatives are available.

Aldehydes are prepared from certain polyhydroxy compounds by the removal of water. For example, furfural is prepared almost exclusively by the action of dilute sulfuric acid on pentosans, such as occur in corncobs, oat hulls, etc. Similarly, unsymmetrical diphenyl ethylene glycol is converted to diphenyl acetaldehyde by boiling with 20% sulfuric acid. In the same manner acrolein is obtained by the dehydration of glycerol with alkali sulfates, or other salts.

Grignard Reagent

If formic acid is considered as hydroxy-formaldehyde, it may serve to explain the reaction of certain derivatives, such as ethyl formate, orthoformic ester, chloroformamide, and disubstituted formamides, with the Grignard reagent to form aldehydes of the type RCHO, where the R group is derived from the Grignard reagent. This reaction is very general in application but also very expensive.

A unique but nevertheless important reaction because it results in the commercial production of one of the higher aliphatic aldehydes is the thermal decomposition of castor oil to give n-heptaldehyde along with undecylenic acid and acrolein.

Friedel-Crafts' Reactions

Certain of the common methods for preparing aldehydes are useful only in the aromatic series. The greater number of these may be classed as modified Friedel and Crafts' reactions. The simplest case is the addition of carbon monoxide to benzene in the presence of aluminum chloride, to form benzaldehyde. If high pressures are used, the additional catalyst, cuprous chloride, is unnecessary and in certain polymethyl benzenes, zinc chloride may be used as the condensing agent.

Another very general method, attributed to Gatterman, involves the use of hydrogen chloride and hydrogen cyanide with a catalyst, such as aluminum chloride or zinc chloride. It is especially useful for preparing phenolic aldehydes or their ether derivatives. Like the Friedel-Crafts' reaction, its usefulness is restricted somewhat to aromatic compounds containing ortho and para directing substituents. An additional disadvantage is the extremely poisonous nature of the reagent, liquid hydrogen cyanide. Adams has overcome this danger to some extent by using zinc cyanide as the condensing reagent, and Karrar also has modified this method by using cyanogen bromide instead of hydrogen cyanide. Although the decrease in the toxicity of the reagent is doubtful, the reaction will work very well with the polyhydroxybenzenes.

A method which suggests care in its execution has been developed by Scholl in condensing fulminic acid from mercury fulminate with aromatic hydrocarbons, through the use of hydrated aluminum chloride. The product is an aldoxime which may be hydrolyzed to the benzaldehyde.

Polymethylbenzenes are readily oxidized to the aldehyde by Etard's reaction, which consists of adding chromyl chloride to the hydrocarbon and hydrolyzing the double-addition product thus formed. Meta-tolualdehyde and related compounds are also made in this manner.

Certain negatively substituted toluenes and xylenes may be condensed with nitrosodimethylaniline to form benzylidene derivatives. These are readily hydrolyzed in acid solution to the aldehyde.

NEW EASTMAN ORGANIC CHEMICALS

	3497	5-Aminouracil	10 g.	$ 4.00	C
	3483	n-Butyl Sebacate BP 160-161°/1 mm.	100 g.	8.00	C
	3283	Cyanoacetanilide MP 199-200°	100 g.	7.00	C
	1594	o-Dinitrobenzene MP 116-117°	100 g.	3.00	C
	3486	Ethyl β-Phenyl-α-cyanoacrylate MP 48.5-49.5°	100 g.	5.00	C
	3511	Guaiacol n-Caproate BP 168-170°/15 mm.	100 g.	5.00	C
	3264	β-Naphthoic Acid MP 183-185°	10 g.	2.00	A
	3482	β-Naphthyl Isocyanate MP 55-56°	100 g.	5.00	C
	3484	5-Nitrouracil	100 g.	12.00	C
	3193	Quinolyl Hydrazine MP 141-142°	10 g.	3.00	A
P	3455	Sodium 2-Bromoethanesulfonate (Pract.)	100 g.	7.00	C
T	3513	Sodium Tri-iso-propylnaphthalenesulfonate (Techn.)	1 kg.	3.50	E
	3510	o-Tolyl Isocyanate BP 77-78°/12 mm.	100 g.	6.00	C
	3503	m-Tolyl Isocyanate BP 75-76°/12 mm.	100 g.	7.00	C

PRICE CHANGES

	445	Glycine (ammonia-free) MP 230-235° dec.	1 kg.	$21.00	D
P	445	Glycine (Pract.) MP 225-230° dec.	1 kg.	14.00	E
	830	Triphenylcarbinol MP 162-163°	100 g.	2.50	C
P	830	Triphenylcarbinol (Pract.) MP 152-160°	500 g.	7.50	D

Micro Molecular Weight Determinations

THE freezing point method of determining the molecular weight of organic compounds was described in a previous issue of this Bulletin (Vol. V, No. 1, October, 1931). The growing importance of micro methods in chemistry, however, has led to new procedures, such as the Rast micro method which avoids the use of the Beckmann apparatus.

The Rast micro molecular weight determination is carried out in an ordinary melting point apparatus. About 10 mg. of the substance under investigation are dissolved in ten to twelve times the amount of camphor by melting the two together several times. The freezing point of this solution and that of the camphor used as solvent are then determined by a technic which varies slightly from the usual melting point procedure. Details of the method may be found in the recent English translation of Gattermann-Wieland, *Laboratory Methods of Organic Chemistry*. From the depression found, the molecular weight may be calculated in the usual way. Oddly enough, camphor shows a capillary molecular freezing point constant of 40, rather than the higher value, 49.5, found by macro methods.

Oftentimes, however, a compound is not soluble in camphor, or may be associated in it. Pirsch, of Vienna, has found that compounds with a similar structure to that of camphor, i.e., camphanes—where a bicyclic structure with a $>C(CH_3)_2$ bridge connecting the 1.4 positions is present—have high freezing point constants, and may be used in place of camphor. Some of the compounds which he has described in a series of articles appearing in the *Berichte* are listed in the accompanying table. The ratio of freezing point constant to molecular weight, C/M.W., serves as a useful means of comparison. In the series given, the relation is extraordinarily high when compared to the value for benzene and acetic acid (0.065).

The generalization that the $>C(CH_3)_2$ bridge in the 1.4 position is essential has been tested by examining the compounds, trans-dipentene-bishydrochloride and -bishydrobromide, and dipentene tetrabromide. All three have low freezing point constants and the C/M.W. values are of the order of 0.043. These studies are still in the development stage, but for ordinary use the five compounds, borneol, camphene, camphor, pinene hydrochloride, and pinene dibromide, are wholly satisfactory.

Compounds of the camphane type might be used with success in the determination of the molecular weight by the cooling curve method. Camphene suggests itself as a suitable solvent in such procedure, but its high volatility might militate against its use. Another possibility is *d*-camphor oxime (m.p. 114-116). Since the cooling curve method is not a micro method, the depression constants would have slightly different values. The evaluation of the constants and subsequent employment in a determination would constitute an interesting student investigation.

COMPOUND	F.P.	M.W.	C*	C/M.W.
Borneol	204°	154.1	35.8	0.232
Camphene	49°	136.1	31.1	0.228
Camphor	174°	152.1	40.0	0.263
Pinene Dibromide	170°	296.0	80.9	0.273
Pinene Hydrochloride	148°	172.6	45.4	0.263

** Values apply only to micro determinations.*